

Potential of Chevrel Phases for Thermoelectric Applications

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ABSTRACT. A low lattice thermal conductivity is one of the requirements to achieve high thermoelectric figures of merit. Several low thermal conductivity materials were identified and developed over the past few years at the Jet Propulsion Laboratory (JPL), including filled skutterudites and Zn_4Sb_3 -based materials. A study of the mechanisms responsible for the high phonon scattering rates in these compounds has demonstrated that materials with structures that can accommodate additional atoms in their lattice are likely to possess low lattice thermal conductivity values. Chevrel phases (Mo_6Se_8 -type) are just such materials and are currently being investigated at JPL for thermoelectric applications. The crystal structures of the Chevrel phases present cavities which can greatly vary in size and can contain a large variety of atoms ranging from large ones such as Pb to small ones such as Cu. In these materials, small inserted atoms usually show large thermal parameters which indicate that they move around and can significantly scatter the phonons. The electronic and thermal properties of these materials can potentially be controlled by a careful selection of the filling element(s). We have synthesized $(\text{Cu}, \text{Cu/Fe}, \text{Ti})_x\text{Mo}_6\text{Se}_8$ samples and report in this paper on their thermoelectric properties. Approaches to optimize the properties of these materials for thermoelectric applications are discussed.

INTRODUCTION

A growth in the commercial applications of thermoelectric cooling and power generation devices depends primarily on increasing the figure of merit ZT of the materials used in the devices. The figure of merit ZT of the materials is defined as $ZT = \alpha^2 T / \rho \lambda$ where α is the Seebeck coefficient, ρ the electrical resistivity, and λ the thermal conductivity. Although stagnant for most of the last 30 years, the search for advanced thermoelectric materials has undergone a remarkable rebirth over the last several years. This is mostly due to recent studies on many new complex materials which were not investigated for thermoelectric applications. Efforts to identify new classes of advanced thermoelectric materials initiated at the Jet Propulsion Laboratory (JPL) in 1991 have resulted in the discovery of several materials with superior thermoelectric properties, including skutterudites and Zn_4Sb_3 -based materials [1-3]. Several new

other approaches for developing advanced materials have been recently reviewed [4]. An obvious requirement for achieving high thermoelectric figures of merit is a low lattice thermal conductivity. One of the new concepts to develop low lattice thermal conductivity materials is to look at compounds which can be referred to as “rattling” semiconductors. The idea was originally proposed by Slack [5] who suggested that, in crystals containing loosely bound atoms, phonons should be scattered more strongly than electrons (holes). This concept has been successfully demonstrated for the skutterudite class of materials [3, 6-8].

Ternary chalcogenides of formula $M_x\text{Mo}_6\text{X}_8$ ($M = \text{Cu, Ag, Ni, Fe, rare earth, etc.}$) and $X = \text{S, Se, or Te}$ have been known since the 1970's. They have attracted considerable interest because of their superconducting properties with large critical magnetic fields [9]. They were first synthesized by Chevrel et al. in 1971 [10] and therefore are often referred to as Chevrel compounds. Ternary phases have structures closely related to those of binary molybdenum chalcogenides Mo_6X_8 ($X = \text{S, Se, Te}$). The Mo_6X_8 unit is illustrated in Figure 1 and consists of an $[\text{Mo}_6]$ octahedron “cluster” surrounded by eight chalcogens arranged in a distorted cube.

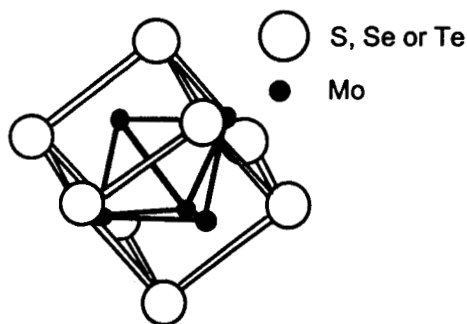


Fig. 1: Illustration of the Mo_6X_8 ($X = \text{S, Se, Te}$) building block of the rhombohedral Chevrel phase structure.

The rhombohedral Chevrel phase consists of a stacking of Mo_6X_8 units and contains channels where additional metal atoms can be inserted, forming $M_x\text{Mo}_6\text{X}_8$ compounds where M can be a variety of atoms from small to large ones ($M = \text{Ag, Sn, Ca, Sr, Pb, Ba, Ni, Co, Fe, Cr, Mn, ...}$; for a complete list see for example [11]). Many of the physical and structural properties of ternary Chevrel phases depend on the size and electronic configuration of the filling atoms. This has been the object of numerous investigations. An excellent review was published by Yvon [9]. Until recently, these materials were not investigated for thermoelectric

applications. We have started to evaluate their potential and reported some results on the electrical and thermal transport properties of the pseudo-binary compound $\text{Mo}_2\text{Re}_4\text{Se}_8$ and $(\text{Fe},\text{Co})_x\text{Mo}_6\text{Se}_8$ filled compounds [12,13]. In particular, we have shown that the insertion of Fe or Co atoms in the voids efficiently scattered the phonons, resulting in room temperature lattice thermal conductivity values around 10 mW/cmK which is comparable to those for state-of-the-art thermoelectric materials which typically are heavily doped semiconductors. Our efforts have recently therefore focused on developing low thermal conductivity semiconducting Chevrel phases, most of which are metallic. We report in this paper on the synthesis and transport properties of Cu, Cu/Fe, and Ti filled Mo_6Se_8 compositions. The results and prospects for improving the thermoelectric properties of these materials are discussed.

EXPERIMENTAL

Single phase, polycrystalline samples of $(\text{Cu}, \text{Cu/Fe}, \text{Ti})_x\text{Mo}_6\text{Se}_8$ were prepared by mixing and reacting stoichiometric amounts of copper (99.999%), iron (99.998%), titanium (99.99%), molybdenum (99.999%), and selenium (99.999%) powders. The powders were first mixed in a plastic vial using a mixer before being loaded into quartz ampoules which were evacuated and sealed. The ampoules were then heated at 1473K for 2 days. A total of three anneals at 1473K for 2 days each and with intermediate crushing and grinding was necessary to obtain single phase materials. The samples were analyzed by x-ray diffractometry (XRD) after each anneal. The powders were then hot-pressed in graphite dies into dense samples, 10 mm long and 6.35 mm in diameter. The hot-pressing was conducted at a pressure of about 20,000 psi and at temperatures between 1123 and 1273 K for about 2 hours under argon atmosphere. The density of the samples was calculated from the measured weight and dimensions and was found to be about 95% of the theoretical density. X-ray diffractometry analysis (XRD) was performed at room temperature on a Siemens D-500 diffractometer using Cu-K_α radiation. Small additions of Si powders were made to the samples as an internal standard. The results show that the samples were composed of about 97% of a phase corresponding to the Mo_6Se_8 structure. Microprobe analysis (MPA) was performed on these samples to determine their atomic composition using a JEOL JXA-733 electron superprobe operating at 20×10^3 Volts (V) of accelerating potential and 25×10^{-9} Amperes (A) of probe current. Samples in the form of disks (typically a 1.0 mm thick, 6.35 mm diameter slice) were cut from the cylinders using a diamond saw

(perpendicular to the pressing direction) for electrical and thermal transport property measurements. All samples were characterized at room temperature by Seebeck coefficient, Hall effect and electrical resistivity measurements. High temperature electrical resistivity, Hall effect, Seebeck coefficient, thermal diffusivity, and heat capacity measurements were also conducted on selected samples between room temperature and about 1100K. Details of the transport properties measurements were previously reported [12].

RESULTS AND DISCUSSION

The room temperature properties of the Cu, Cu/Fe, and Ti filled compositions are listed in Table I.

TABLE I. Some properties of Cu, Cu/Fe, and Ti filled compositions at 300K

	Units	$\text{Cu}_4\text{Mo}_6\text{Se}_8$	$\text{Cu}_2\text{FeMo}_6\text{Se}_8$	TiMo_6Se_8
Microprobe composition	at%	$\text{Cu}_{3.1}\text{Mo}_6\text{Se}_8$	$\text{Cu}_{1.38}\text{Fe}_{0.66}\text{Mo}_6\text{Se}_8$	$\text{Ti}_{0.9}\text{Mo}_6\text{Se}_8$
Conductivity type		p	p	p
Electrical resistivity	m Ω cm	0.84	1.09	6
Seebeck coefficient	$\mu\text{V/K}$	14	16	70
Hall carrier concentration	cm^{-3}	8.8×10^{21}	9×10^{21}	1.8×10^{21}
Hall mobility	cm^2/Vs	0.4	3.6	0.6
Thermal conductivity	mW/cmK	10	10.5	10.2

All samples show p-type conductivity. As we mentioned before, the stacking of Mo_6X_8 units leaves empty channels where additional metal atoms can be inserted. Large atoms such as Pb or La can exclusively occupy the largest of the voids with a filling factor limit corresponding to $x \sim 1$. Smaller atoms such as Cu, Ni or Fe, for example can be inserted in 12 different smaller holes with irregular shapes in the chalcogen channels. Considering geometrical factors, these 12 sites cannot be occupied simultaneously and the theoretical filling limit of 6 metal atoms. For small atoms, the upper occupancy limit was experimentally found to be corresponding to $x=4$. The factor which further limits metal atoms occupancy turns out to be electronic. The number of electrons per Mo atom in the cluster, often referred to as “cluster-valence-electron count” (cluster-VEC) is calculated by adding the valence electrons of M atoms to

the valence electrons of Mo atoms, by subtracting the number of electrons required to “fill” the octets of the chalcogen atoms and dividing the result by the number of Mo atoms [14]. Chevrel phases are formed for cluster VEC numbers between 3.3 and 4. [14]. In addition, band structure calculations results predicted an energy gap in the electronic structure for 4 valence electrons per Mo atom in the cluster [15]. Values of 4 are attained in mixed-metal cluster compounds such as $\text{Mo}_2\text{Re}_4\text{Se}_8$ and $\text{Mo}_4\text{Ru}_2\text{Se}_8$ and these compounds were found to be semiconductors [12,16,17], supporting the idea of an energy gap in the band structure of the Chevrel phases with a “magic” cluster VEC number of 4.

Assuming an oxidation state of 2+ for Fe, 1+ for Cu, and 4+ for Ti, we selected the nominal compositions $\text{Cu}_4\text{Mo}_6\text{Se}_8$, $\text{Cu}_2\text{FeMo}_6\text{Se}_8$, and TiMo_6Se_8 , each of which has a calculated VEC of 4 and should therefore be semiconducting. Microprobe results however show that the degree of filling is less than the nominal value which point to some other limiting factors. It was pointed out by Yvon [9] that there is a difference in the degree of covalency in the sulfides, selenides, and tellurides, the formal charge of Se and Te is smaller than the one for S. Fewer electrons may therefore be needed in the selenides and tellurides to reach a VEC of 4. For the selenides, it was estimated that the formal charge of Se decrease by 1/8 compared to that of S. Assuming a charge of -2 for S, only 3 additional electrons would be needed to achieve a VEC of 4 for selenides and potentially the semiconducting state. Thus, the filling limit is reached for smaller x, consistent with microprobe results (see Table I). In addition, one can speculate that the high temperature annealing required to obtain nearly single phase samples generate defects that can block some of the voids and therefore limit the metal atoms occupancy.

The temperature variations of the electrical resistivity and Seebeck coefficient for $(\text{Cu}, \text{Cu/Fe}, \text{Ti})_x\text{Mo}_6\text{Se}_8$ Chevrel phases are shown in Figures 2 and 3, respectively. The results indicate that the Cu and Cu/Fe filled compositions behave as semimetals while the Ti filled composition shows a semiconducting behavior. This is in agreement with recent band structure calculations [18-20]. The Ti filled composition is the first truly semiconducting ternary phase obtained to date and show some promise with respect to controlling the electronic properties of these materials. The carrier mobility values, as observed for the pseudo-binary compound, are relatively low, resulting in relatively high electrical resistivity values.

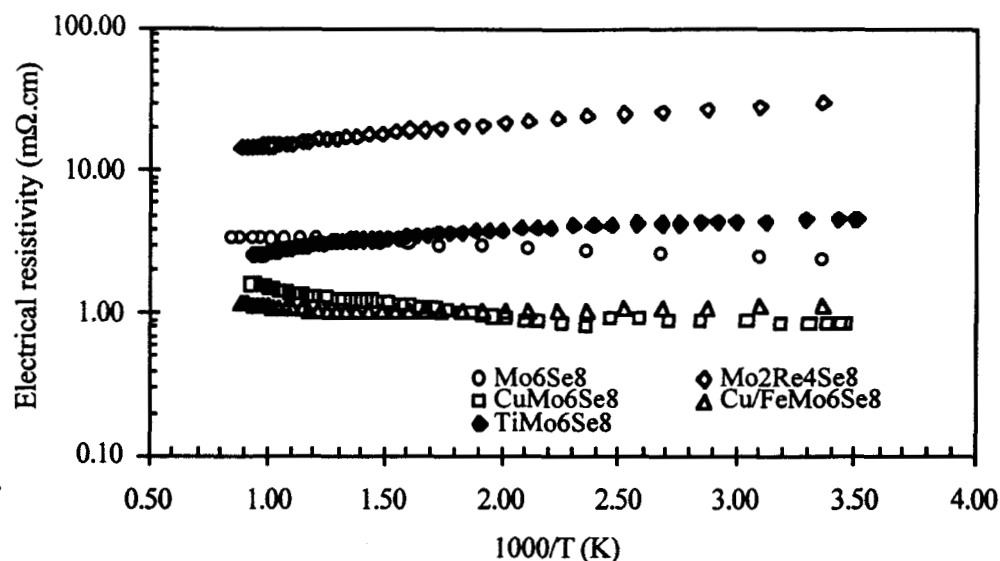


Fig. 2: Electrical resistivity versus inverse temperature for $(\text{Cu}, \text{Cu/Fe}, \text{Ti})_x\text{Mo}_6\text{Se}_8$ Chevrel phases. Data for Mo_6Se_8 and $\text{Mo}_2\text{Re}_4\text{Se}_8$ are also shown for comparison [12].

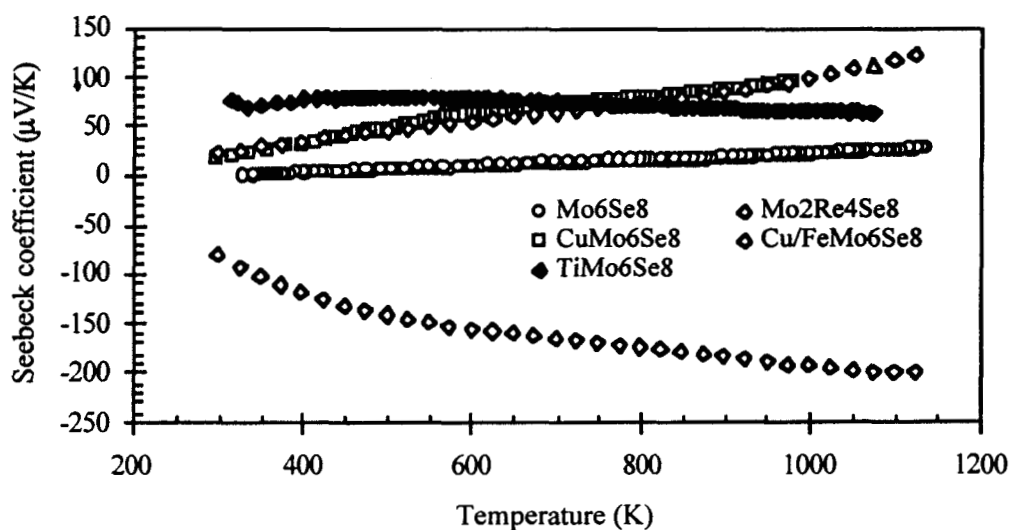


Fig. 3: Seebeck coefficient versus temperature for $(\text{Cu}, \text{Cu/Fe}, \text{Ti})_x\text{Mo}_6\text{Se}_8$ Chevrel phases. Data for Mo_6Se_8 and $\text{Mo}_2\text{Re}_4\text{Se}_8$ are also shown for comparison [12].

Experimental thermal conductivity data are shown in Figure 4. The room temperature thermal conductivity for Mo_6Se_8 is about 70 mW/cmK and the

thermal conductivity decreases with increasing temperature to a minimum value of about 45 mW/cmK at 1100K. For $\text{Mo}_2\text{Re}_4\text{Se}_8$, the thermal conductivity is significantly lower with a room temperature thermal conductivity of 40 mW/cmK. Considering the relatively large electrical resistivity values, the total thermal conductivity shown corresponds to approximately 98% of the lattice contribution. The thermal conductivity varies approximately as $T^{-1/2}$ which is indicative of a phonon scattering by

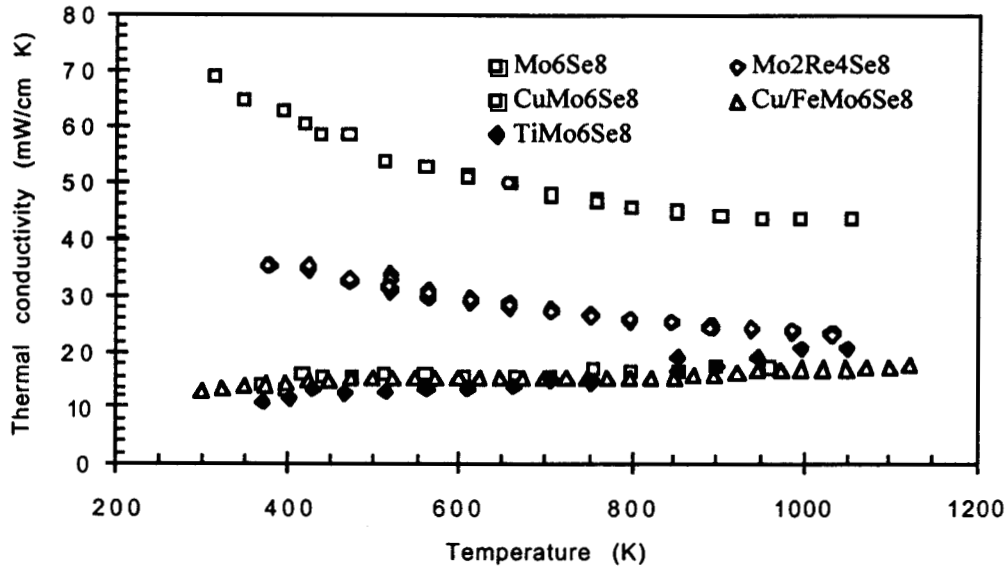


Fig. 4: Thermal conductivity versus temperature for $(\text{Cu}, \text{Cu/Fe}, \text{Ti})_x\text{Mo}_6\text{Se}_8$ Chevrel phases. Data for Mo_6Se_8 and $\text{Mo}_2\text{Re}_4\text{Se}_8$ are also shown for comparison [12].

point defects introduced by the substitution of Re for Mo atoms. A remarkable decrease in thermal conductivity is obtained for $(\text{Cu}, \text{Cu/Fe}, \text{Ti})_x\text{Mo}_6\text{Se}_8$ ternary compositions. The room temperature thermal conductivity is about 13 mW/cmK for these compositions and the thermal conductivity rises with increasing temperature similarly to glass-like materials. As we pointed out before, these compositions are semi-metallic and one can expect a significant charge carrier-phonon scattering which should lower the lattice thermal conductivity. However, it is known that this type of phonon scattering cannot lead to a glass-like behavior for the thermal conductivity and therefore the strong decrease in the thermal conductivity can predominantly be attributed to the “rattling” of the Cu, Fe or Ti atoms in the voids of the Chevrel structure. A measure of the effectiveness of the void filler in scattering phonons is the thermal parameter which is a measure of the ability of the ion to “rattle” inside the

cage. Thermal parameters for some atoms in ternary compounds are listed in Table II. The data show that the thermal parameter in the direction perpendicular to the ternary axis for small atoms is about two order of magnitude larger than those for large atoms such as La or Sn and also those for Mo and Se atoms. The large thermal parameters of the small atoms correlate our findings of low lattice thermal conductivity for $(\text{Cu, Cu/Fe, Ti})_x\text{Mo}_6\text{Se}_8$.

Table II. Thermal vibration parameters for several atoms in $\text{M}_x\text{Mo}_6\text{Se}_8$ ternary compositions (after [12]).

Element and filling fraction	Thermal parameter \perp ternary axis (\AA^2)	Thermal parameter // ternary axis (\AA^2)
$\text{Cu}_{1.0}$	0.869	~ 0
Ag	0.144	0.004
$\text{Sn}_{0.8}$	0.052	0.085
$\text{La}_{0.8}$	0.005	0.013
Mo	0.007	0.006
Se	0.014	0.011

The best calculated ZT value is for the Cu/Fe filled composition with a ZT of 0.6 at 1150K. This value is comparable to those obtained for Si-Ge alloys in the same temperature range. This is an encouraging result considering that further improvement seems possible. Larger Seebeck coefficients can be obtained for semiconducting ternary compositions such as $\text{Ti}_{0.9}\text{Mo}_6\text{Se}_8$. Combined with a low lattice thermal conductivity and potentially tunable electronic properties, these compositions are attractive for thermoelectric applications. All compositions prepared to date have however shown relatively low carrier mobility which will need some improvement in order to achieve thermoelectric figures of merit larger than those obtained for state-of-the-art materials. Work is currently underway to answer some of these questions and fully assess the potential of Chevrel phases for thermoelectric applications.

CONCLUSION

As part of an ongoing search for thermoelectric materials with superior properties, we have started to investigate the transport properties of Chevrel phases. These materials possess voids in their crystal structure

which can be filled with a variety of atoms. Results obtained on several ternary selenide Chevrel phases filled with small atoms such as Cu, Cu/Fe, and Ti show that these atoms are scattering efficiently phonons, significantly reducing the lattice thermal conductivity compared to their binary and pseudo-binary analogs. The electronic properties of the ternary phases are sensitive to the filling fraction and electronic structure of the filling ion. For the first time, a semiconducting filled composition, $\text{Ti}_{0.9}\text{Mo}_6\text{Se}_8$ was prepared and its properties measured. Results to date show that semiconducting compositions with low lattice thermal conductivity can be prepared but further work is needed to fully assess the potential of Chevrel phases for thermoelectric applications. In particular, the issue of low carrier mobility, common to all compositions prepared to date, must be addressed by both theoretical and experimental approaches in order to select the most promising compositions for further investigation.

ACKNOWLEDGMENTS

The work described in this paper was carried out at the Jet Propulsion Laboratory/California Institute of Technology, under contract with the National Aeronautics and Space Administration. The authors would like to thank Dr. A. Borshchevsky, Dr. I. Mazin, Dr. D. J. Singh, and Prof. Glen A. Slack for many helpful discussions. This work is supported by the U. S. Defense Advanced Research Projects Agency, Grant No. E407.

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